Chemical Engineering Journal 300 (2016) 169–176

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Catalytic ozonation of sulfamethazine using $Ce_{0.1}Fe_{0.9}OOH$ as catalyst: Mineralization and catalytic mechanisms

Zhiyong Bai [a,b], Qi Yang [a], Jianlong Wang [b,c,*]

[a] School of Water Resources and Environment, China University of Geosciences, Beijing 100083, PR China
[b] Collaborative Innovation Center for Advanced Nuclear Energy Technology, INET, Tsinghua University, Beijing 100084, PR China
[c] Beijing Key Laboratory of Radioactive Waste Treatment, INET, Tsinghua University, Beijing 100084, PR China

HIGHLIGHTS

- Ce substituted goethite ($Ce_{0.1}Fe_{0.9}OOH$) was prepared by isomorphous substitution method.
- The mineralization efficiency of SMT was enhanced obviously by addition of catalyst.
- Main intermediates were quantified and compared at acidic or basic conditions.
- The possible pathways for SMT degradation by catalytic ozonation were proposed.

ARTICLE INFO

Article history:
Received 7 February 2016
Received in revised form 27 March 2016
Accepted 24 April 2016
Available online 25 April 2016

Keywords:
Catalytic ozonation
Sulfamethazine
Goethite
Antibiotics

ABSTRACT

Ce substituted goethite ($Ce_{0.1}Fe_{0.9}OOH$) was prepared by isomorphous substitution method and used for the catalytic ozonation of sulfamethazine (SMT). The results showed that acidic and neutral pH is beneficial for SMT mineralization. The mineralization efficiency of SMT was enhanced obviously in the presence of catalyst. Major degradation products of SMT during catalytic ozonation process were quantified and compared at acidic or basic conditions. Among the intermediates, 2-amine-4,6-dimethylpyrimidin accounted for high proportion. The small-molecule organic acids accumulated, which can inhibit the degradation reaction by lowering solution pH value. Based on the competitive degradation results of the intermediates and SMT, the possible pathways for SMT degradation by catalytic ozonation were tentatively proposed.

1. Introduction

Sulfonamides are widely and extensively used as antibacterial drugs and growth promoters, especially in China [1]. After their usage, large amount of them are excreted in urine or feces due to their incomplete metabolism. They have been detected in surface water, underground water, and the effluent of wastewater treatment plants [2]. Although their concentration levels are generally in the range of nanograms to micrograms per liter, they could damage ecological environment and public health [3,4].

Sulfamethazine (SMT) is a typical sulfonamide, which contains a sulfanilamide group. Due to its inhibition to the most Gram-positive and many Gram-negative bacterial growth [5], the conventional biological wastewater treatment process is not effective for the removal of SMT. In recent years, chemical oxidation methods, especially the advanced oxidation processes (AOPs), have been used for degradation of SMT, including photo-catalytic method [1,6], Fenton and Fenton-like process, electro catalysis [7], gamma irradiation [8,9] and ozonation [10].

Heterogeneous catalytic ozonation is effective for removing toxic pollutants from wastewater. The mechanisms for heterogeneous catalytic ozonation system include the transformation of ozone into more reactive species, and/or through adsorption ozone and pollutant molecules onto the surface of the catalyst to promote the mass-transfer efficiency.

In recent years, composite iron oxides have been widely used as the catalyst of ozonation, due to their stable structure, high oxygen vacancies and high density of surface hydroxyl groups [11–14]. For example, $CuFe_2O_4$ was used for catalytic ozonation of phenacetin (PNT) [15]; $MnFe_2O_4$ was prepared and used as catalyst, which was highly effective in catalyzing ozone decomposition and favorable to generate more hydroxyl radicals [12]; silicon-modified ferric hydroxide was beneficial to the enhancement of nitrobenzene degradation compared with ozonation alone [16].

* Corresponding author at: Neng Ke Lou, Tsinghua University, Beijing 100084, PR China.
E-mail address: wangjl@tsinghua.edu.cn (J. Wang).

http://dx.doi.org/10.1016/j.cej.2016.04.129
1385-8947/

Iron oxyhydroxides (FeOOH) are common crystalline forms of iron, which play an important role in catalysis through a series of reduction–oxidation reactions. In this study, Ce substituted goethite ($Ce_{0.1}Fe_{0.9}OOH$) was prepared and used for catalytic ozonation of SMT. The main contents were: (1) to determine the major influencing parameters, including pH, ozone concentration, catalyst dosage and initial SMT concentration; (2) to quantify and compare the kinds and concentrations of the intermediates at different conditions; (3) to compare the competitive degradation of the intermediates and to propose the possible degradation pathway of SMT.

The objective of this study is to deepen the understanding of the mineralization process of SMT in catalytic ozonation system.

2. Materials and methods

2.1. Chemicals and reagents

Chemicals used in this study were purchased from Sinopharm Chemical Reagent Co. Ltd, (China), including tert-butyl alcohol (TBA), $Fe(NO_3)_3{\cdot}9H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$, NaOH. SMT and possible intermediates, including sulfaguanidine, hydroquinone sulfanilic acid, 2-amino-4,6-dimethylpyrimidine, and p-aminophenol were purchased from Alfa Aesar Company with purity >99%. All solutions used in this study were prepared with deionized water.

2.2. Preparation of catalyst

The catalyst was prepared by mixing 100 mL solution A: ($Fe(NO_3)_3{\cdot}9H_2O$ and $Ce(NO_3)_3{\cdot}6H_2O$ with total Fe and Ce concentration of 0.53 M) and 350 mL solution B: 2 M NaOH. The reaction was occurred under vigorously magnetic stir for about 30 min. Then, the precipitates were added into a 1-L Teflon bottle, deionized water was added to reach a final NaOH concentration of 0.3 M. The suspensions were aged at 60 °C for 15 days. Bottle was opened daily, and shaken by hand for 10–20 s. Finally, the products were washed and dried in a vacuum freeze dryer overnight. X-ray diffraction (XRD) results were obtained from diffractometer (D8-Advance, Bruker). Morphological properties and the composition of catalyst were recorded by a SEM (Hitachi S-4800) with an energy dispersive X-ray (EDX).

2.3. Degradation experiments

A 3S-A3 laboratory ozonizer (Tonglin Technology, China) was used to provide ozone gas. The ozone concentrations in the inlet and outlet were monitored by an ozone analyzer (BMT 963, Germany). The ozone concentration was controlled by adjusting the power of ozonizer. A 1.2-L cylindrical glass reactor was used in the experiments, in which a certain amount of catalyst was added together with 1 L SMT solution followed by continuously bubbling of ozone gas. Usually, ozone concentration was 15 mg/L, catalyst dosage was 0.2 g/L and SMT concentration was 20 mg/L. The solution was stirred by a magnetic stirrer. At a certain time intervals, samples were taken and filtered for analysis.

Six possible intermediates (sulfaguanidine, 2-amine-4,6-dimethylpyrimidin, sulfanilic acid, sulfanilamide, p-aminophenol and hydroquinone) and five small-molecule organic acids (formic, acetic, propionic, oxalic and butyric acids) were used as standard sample based on the reported intermediates produced by chemical oxidation of SMT [2,8,17,18]. Competition degradation experiments were performed by mixing six intermediates and SMT (individual concentration was 10 mg/L) with conditions of pH 7, ozone concentration 15 mg/L and catalyst dosage 0.2 g/L. The concentration of SMT was calculated from the stand cure which was draw by the relationship between peak area and concentration. For intermediates, the retention time were first confirmed by testing standard solutions, the corresponding peak area were straightly used to represent the change of their contents.

2.4. Analytical methods

The concentration of SMT and the intermediates was quantified by high-performance liquid chromatography (HPLC) (Agilent 1200 Series, DAD detector and XDB-C18 column), using a mixture of acetonitrile and 0.025 mol/L acetic acid (1:9, by volume) at pH 4 as mobile phase, the injection volume was 80 μL. Total organic carbon (TOC) were measured by a Multi TOC/TN Analyzer (2100, Analytik Jena. Germany). Ion chromatograph (Dionex model ICS 2100) were used to measure small-molecule organic acids produced from SMT degradation.

3. Results and discussion

3.1. Characterization of catalysts

Fig. 1 showed the X-ray diffraction patterns of $Ce_{0.1}Fe_{0.9}OOH$, the diffraction peak at 2θ values of 21.29 (110), 33.01 (130), 36.39 (111), 39.62 (121), 41.31 (140), 53.01 (221) and 58.19 (151) plans were associated with the characteristic peaks of goethite (JCPDS Card No. 29-0713). This results proved the prepared catalyst is consist of goethite, and there are no cerium dioxide peak in the catalyst. So we inferred the isomorphous substitution successfully happened.

SEM image and the EDS results in Fig. 2 illustrated the morphology and composition of the synthesized $Ce_{0.1}Fe_{0.9}OOH$. Acicular-like structure particles can be seen in the picture. The length of $Ce_{0.1}Fe_{0.9}OOH$ particles is between 1.00 and 2.00 μm, and the width is spread from 0.10 to 0.40 μm. In order to test the composition of the obtained metal oxide, two part regions of catalyst were choose for EDX test. Results showed a good agreement with the theoretical value, the atomic ratio of iron and cerium is nearly 9:1. Moreover, the iron content in the center is a little higher than in the edge of crystal. The results further proved that the cerium was successfully doped in the goethite.

3.2. Effect of initial pH on SMT mineralization

For ozonation process, the solution pH is an important parameter, which can be influenced by surface properties of catalyst,

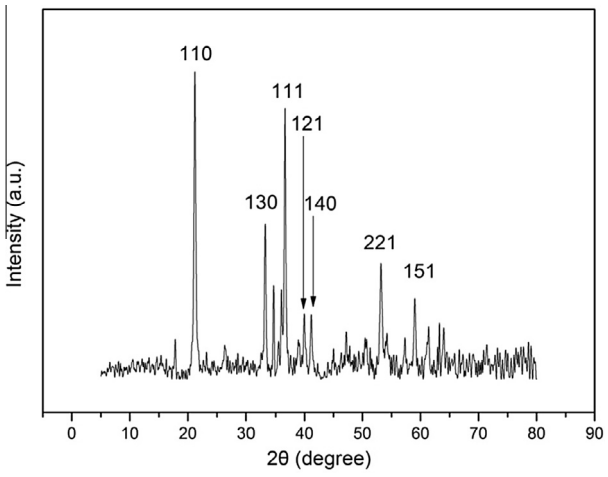

Fig. 1. XRD image of catalyst.